

General Disclaimer

One or more of the Following Statements may affect this Document

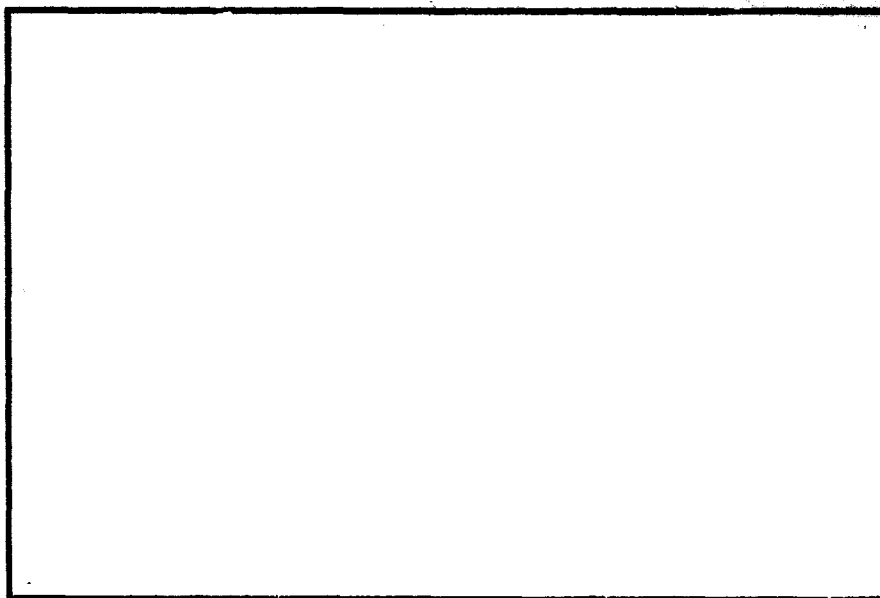
- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

(NASA-CR-169456) SURFACE ANALYSIS IN
COMPOSITE BONDING Semiannual Technical
Report (Virginia Polytechnic Inst. and State
Univ.) 12 p HC A02/MF A01 CSCL 11A

N83-10196

Unclass

G3/27 38376



Virginia Polytechnic Institute
and State University

Blacksburg, Virginia 24061

SEMI-ANNUAL TECHNICAL REPORT

SURFACE ANALYSIS IN COMPOSITE BONDING

by

✓ D. L. Messick and J. P. Wightman

Prepared for

National Aeronautics and Space Administration

October, 1982

✓ Grant NAG-1-248

NASA-Langley Research Center
Hampton, Virginia 23665
Materials Division
Donald J. Progar

Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

INTRODUCTION

There is a continuing need to establish the role of the interfacial region in determining the bond strength and durability of composite bonds. We have reported (1,2) preliminary studies on the characterization of a variety of carbon fibers including Celion 6000 using both scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS or ESCA).

Indeed, Donnet has emphasized recently (3) the importance of the surface characterization of fibers in attempting to understand the properties of composites. However, in the present research, the emphasis is on composite bonding, that is, the adhesive bonding between composites in contrast to fiber-matrix interaction. The primary objective of the research is the characterization of composite surfaces before adhesive bonding and after fracture of bonded specimens. This report details work done on the analysis of composite samples pretreated in a number of ways prior to bonding.

EXPERIMENTAL

A. Samples. Twelve composites prepared from Celion 6000 carbon fibers and a polyimide (LARC-160) were received from the NASA-Langley Research Center. The composite set consisted of an untreated sample and eleven pretreated samples as listed in Table I. A 0.5 cm diameter sample was punched from each composite panel and photographed at 20X with a Bausch and Lomb optical microscope prior to any analysis. The untreated sample designated #1A delaminated on punching and hence a virgin internal surface was produced and designated #1B.

B. X-ray Photoelectron Spectroscopy (XPS). XPS studies of the composites were obtained with a Physical Electronics SAM 550 spectrometer using a Mg X-ray

anode. The spectrometer is located at Poly-Scientific in Blacksburg. Punched samples were mounted to the XPS stage with double-sided tape. A wide scan of binding energies (0 to 1000 eV) was performed on Samples 1A and 1B initially. Subsequent narrow scans were completed for the elements C, N, O, S, F, Al, Si, and K on all samples. The atomic fraction of each of these elements present in the top 5 nm of the surface was calculated.

C. Scanning Electron Microscopy (SEM). After obtaining XPS data, scanning electron microscopy (SEM) was performed on either an Advanced Metals Research Model 900 scanning electron microscope or a JEOL JSM-35-C scanning electron microscope. Samples observed in the former microscope were coated with a Au/Pd alloy in a Denton vacuum evaporator Model DV515. Remaining samples were coated with Au prior to observation. All sample surfaces were photographed at 20X initially. Detailed photomicrographs of characteristic and unique areas of the surface followed for each sample, in some cases to a magnification of 2000X.

D. Contact Angles. Five different liquids of varying surface tensions were used for contact angle determinations. The liquids and respective surface tensions (in mJ/m²) are noted below: water (72.8), formamide (58.3); methylene iodide (50.8); bromonaphthalene (44.6); n-hexadecane (27.6). A droplet of each liquid approximately 5 mm (diameter) was placed on each composite sheet. Contact angles were measured with a Gaertner Scientific goniometer within 30 seconds after the introduction of the droplet. A second replication was completed for each liquid on each composite.

Data reduction of the measured contact angle(θ)-surface tension (γ) results was done using the University IBM 1360 System. Critical surface tensions for each composite were obtained by extrapolation of $\cos \theta$ vs γ plots.

RESULTS AND DISCUSSION

Research accomplished during this report period is summarized in Table I. Composite samples studied by particular techniques are indicated by X.

A. Scanning Electron Microscopy (SEM). SEM photomicrographs were used to assess changes in surface topography of composite samples after different pretreatments. Indeed, the mechanical pretreatments (Sample Nos. 2-6) appeared to "break into" the fibers in contrast to the chemical pretreatments (Nos. 7-9). Representative SEM photomicrographs will be included in the Final Technical Report.

B. X-ray Photoelectron Spectroscopy (XPS or ESCA). An extensive XPS study was done on the composite samples before and following different pretreatments. Wide scan XPS spectra were obtained on Samples Nos. 1A, 1B, 7, 8, and 9. The major photopeaks were assigned to fluorine, oxygen, nitrogen and carbon. The presence of large amounts of fluorine on the surface of some of the samples even after pretreatment is a striking result and emphasizes the importance of surface analysis. In addition, trace amounts of calcium and sodium were noted on Sample No. 7 and Nos. 1A and 7, resp. Aluminum, silicon and gold were detected on some samples. It is presumed that these elements are associated with the sample holder and further work is in progress to check this point.

Narrow scan XPS spectra were obtained on all samples and in addition to scanning for fluorine, oxygen, nitrogen and carbon, scans were also made for potassium, sulfur, aluminum and silicon. These latter elements were suspected surface impurities based on the known pretreatments. Potassium was not detected on any sample; sulfur appeared as a trace impurity but it may be associated also with the sample holder.

The quantitative results of the XPS analysis are given in Tables II and

III. The binding energies (B.E.) in eV and the atomic fractions (A.F.) for the F 1s, O 1s, N 1s and C 1s photopeaks are listed in Table II. Half of the samples contained high concentrations of surface fluorine even following pretreatment and in every case, a high binding energy photopeak around 292 eV was observed in the C 1s spectrum. This is a characteristic of carbon-fluorine bonding (4). Of particular interest is the fact that the as-received or untreated composite sample(#1A) has a large fluorine signal. However, the fluorine photopeak is some 100 times smaller for a freshly exposed surface (#1B) produced on delamination of the same sample.

The atomic fraction ratios are listed in Table III. There are large differences in the F/C ratio for the various samples. The mechanically pretreated composites generally have lower F/C ratios than the chemically pretreated composites. The longer Flashblast treated samples show a much reduced fluorine signal. Further, the values of the O/C ratio are fairly constant except for the Flashblast pretreated Sample Nos. 11, 12 and 12W. A parallel trend is noted in the N/C ratio. It appears as though the Flashblast pretreatment carbonizes the surface region resulting in the removal of oxygen and nitrogen contained in gaseous species possibly, for example, CO and HCN.

In summary, the surface fluorine is associated with the external composite surfaces only which suggests the inclusion of fluorine during molding. The order of removal of the surface fluorine species is longer Flashblast > mechanical > chemical.

Fracture studies at NASA-LARC (5) have been made on similar composites pretreated in the same ways as above. The effect of surface contamination on bond strength is being evaluated currently.

C. Critical Surface Tension. The critical surface tension of each composite sample is listed in Table IV. The critical surface tension was

determined using the Zisman approach (6). A direct correlation is suggested between the surface fluorine concentration as measured by XPS and the value of the critical surface tension. The results of these two independent techniques are plotted in Figure 2. Indeed, the higher the surface fluorine concentration, the lower the critical surface tension. This result is consistent with critical surface tensions reported for fluoropolymers (7).

REFERENCES

1. W. Chen and J. P. Wightman, "A Fundamental Approach to Adhesion: Synthesis, Surface Analysis, Thermodynamics and Mechanics", NASA Report NSG-1124, NASA-LARC, Hampton, VA, January, 1979.
2. W. Chen and J. P. Wightman, Proc. 14th Biennial Conference on Carbon, P. A. Thrower, Ed., p. 107, State College, Pa. (1979).
3. J. B. Donnet, Abstracts, 4th Intl. Conference on Surface and Colloid Science, Jerusalem, July, 1981.
4. K. Siegbahn et al., "ESCA-Atomic, Molecular and Solid State Structure Studies by Means of Electron Spectroscopy", Almquist and Wiksells, Upsalla (1967).
5. D. J. Progar, communication, August, 1982.
6. W. A. Zisman in "Contact Angle, Wettability and Adhesion", Adv. Chem. Series #43, R. F. Gould, Ed., pp. 1-51, Am. Chem. Soc., Washington (1964).
7. *ibid*, p. 16.

TABLE I

SUMMARY OF RESEARCH DONE ON COMPOSITES

Sample No.	Sample Pretreatment	Technique				
		Punched	OM	SEM	XPS	CA
1A	As received	X	X	X	X	X
1B	Delaminate	X	X	X	X	X
2	120 Al ₂ O ₃ Grit Blasted	X	X	X	X	X
3	Boeing Grit Blasted	X	X	X	X	X
4	Glass Bead Blast	X	X	X	X	X
5	600 SiC Handsanded	X	X	X	X	X
6	180 SiC Handsanded	X	X	X	X	X
7	Ethanol KOH	X	X	X	X	X
8	NH ₂ NH ₂ ·H ₂ O	X	X	X	X	X
9	Conc. H ₂ SO ₄ + 30% H ₂ O ₂	X	X	X	X	X
10	Flashblast #1	X	X	X	X	X
11	Flashblast #2	X	X		X	X
12	Flashblast #3	X	X		X	X
10W	Flashblast #1 after washing (MeOH)					X
11W	Flashblast #2 after washing					X
12W	Flashblast #3 after washing	X			X	X

OM - Optical Microscopy; SEM - Scanning Electron Microscopy;
 XPS - X-ray Photoelectron Spectroscopy; CA - Contact Angle

TABLE II

XPS ANALYSIS OF COMPOSITES

Sample No.	Photopeak				
	F 1s	O 1s	N 1s	C 1s	
1A	689.0 0.19	531.8 0.11	399.8 0.030	(284.6) 0.66	B.E. A.F.
1B	688.8 0.002	532.4 0.11	400.2 0.020	(284.6) 0.86	
2	689.0 0.13	531.4 0.11	399.8 0.020	(284.6) 0.73	
3	689.0 0.060	532.0 0.15	400.0 0.023	(284.6) 0.75	
4	689.2 0.12	531.8 0.12	400.0 0.024	(284.6) 0.73	
5	689.4 0.025	532.2 0.13	400.2 0.020	(284.6) 0.80	
6	689.0 0.027	531.8 0.12	400.0 0.032	(284.6) 0.81	
7	689.2 0.26	531.8 0.10	399.8 0.012	(284.6) 0.63	
8	689.2 0.20	531.8 0.10	399.6 0.041	(284.6) 0.64	
9	689.2 0.19	532.0 0.12	400.0 0.020	(284.6) 0.66	
10	689.4 0.14	532.0 0.080	400.2 0.026	(284.6) 0.74	
11	- NSP	532.6 0.053	- NSP	(284.6) 0.93	
12	689.2 0.006	532.4 0.078	400.0 0.010	(284.6) 0.89	
12W	- NSP	532.4 0.071	400.0 0.021	(284.6) 0.89	

TABLE III

XPS ATOMIC RATIOS FOR COMPOSITES

Sample No.	Atomic Fraction Ratio		
	F/C	O/C	N/C
1A	0.29	0.17	0.145
1B	0.0023	0.13	0.023
2	0.18	0.15	0.027
3	0.08	0.20	0.031
4	0.16	0.16	0.032
5	0.031	0.16	0.025
6	0.033	0.15	0.040
7	0.41	0.16	0.019
8	0.31	0.16	0.064
9	0.29	0.18	0.030
10	0.19	0.11	0.035
11	<0.001	0.057	<0.001
12	0.0067	0.088	0.011
12W	<0.001	0.080	0.023

TABLE IV

CRITICAL SURFACE TENSIONS OF COMPOSITES

<u>Sample No.</u>	<u>Critical Surface Tension (mJ/m²)</u>
1A	23
2	31
3	37
4	33
5	35
6	40
7	23
8	28
9	31
10	37
11	40
12	40.5

ORIGINAL PAGE IS
OF POOR QUALITY

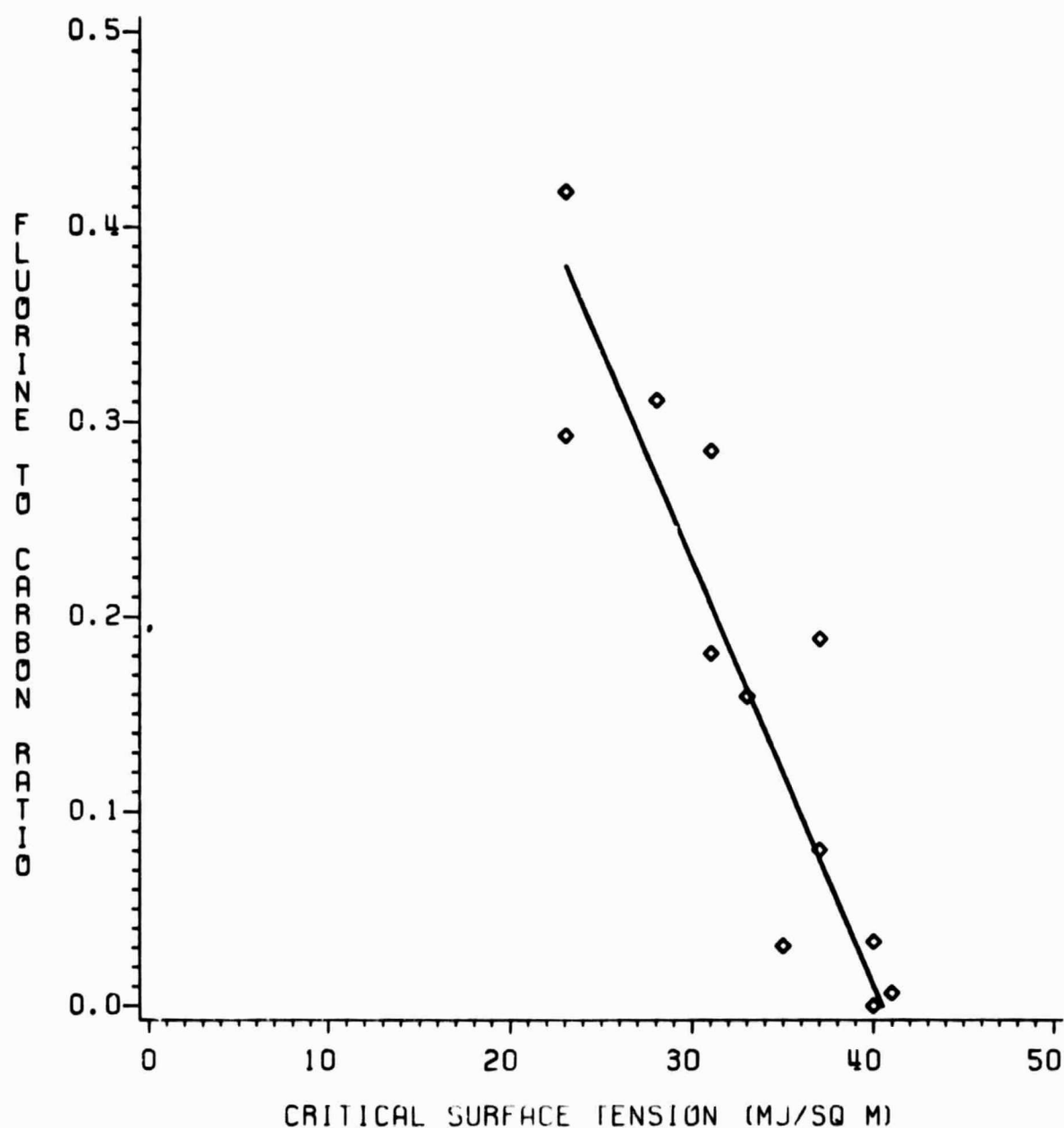


FIG. 1 -CHANGES IN THE RATIO OF FLUORINE TO CARBON
AS RELATED TO THE CRITICAL SURFACE TENSION
MEASURED IN MILLIJOULES PER SQUARE METER